# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188



| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE | 3. DATES COVERED (From - To) |
|---|---|---|
| 30-09-2013 | Final Report | 1-Jul-2012 - 30-Jun-2013 |

**4. TITLE AND SUBTITLE**
Investigating the Mechanisms and Potential of Silk Fiber Metallization

**5a. CONTRACT NUMBER**
W911NF-12-1-0200

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**
611102

**6. AUTHORS**
David Breslauer

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAMES AND ADDRESSES**
Refactored Materials, Inc.
344a Prentiss St

San Francisco, CA 94110 -6141

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

**10. SPONSOR/MONITOR'S ACRONYM(S)**
ARO

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
61780-LS.1

**12. DISTRIBUTION AVAILIBILITY STATEMENT**
Approved for Public Release; Distribution Unlimited

**13. SUPPLEMENTARY NOTES**
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

**14. ABSTRACT**
The metallization of fibers and textiles using Atomic Layer Deposition (ALD) has been of increasing interest for its ability to create novel material surface properties, create conductive materials, and otherwise functionalize materials. In 2009, it was shown that through modification of the ALD process, metal elements could be infiltrated within (rather than simply coating) biological materials. This metal infiltration was shown to dramatically enhance the mechanical properties of biological materials1. Native spider silk fibers are unparalleled in their combination of

**15. SUBJECT TERMS**
silk, spider, fiber, ALD, metallization, metal infiltration

| 16. SECURITY CLASSIFICATION OF: a. REPORT | b. ABSTRACT | c. THIS PAGE | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| UU | UU | UU | UU | | David Breslauer |
| | | | | | 19b. TELEPHONE NUMBER |
| | | | | | 510-703-0967 |

## Report Title

Investigating the Mechanisms and Potential of Silk Fiber Metallization

## ABSTRACT


The metallization of fibers and textiles using Atomic Layer Deposition (ALD) has been of increasing interest for its ability to create novel material surface properties, create conductive materials, and otherwise functionalize materials. In 2009, it was shown that through modification of the ALD process, metal elements could be infiltrated within (rather than simply coating) biological materials. This metal infiltration was shown to dramatically enhance the mechanical properties of biological materials1. Native spider silk fibers are unparalleled in their combination of mechanical strength and strain, and these fibers exhibited >2-fold increase in strain to breakage, and >4.5-fold increase in strength when infiltrated with zinc, titanium, or aluminum. Unfortunately, the mechanisms leading to this mechanical improvement, and the limits thereof, have been largely unexplored. This is due to an inability to replicate to the initial results of the 2009 work by independent labs. We sought to replicate the original work, and to investigate the molecular mechanisms underlying the metallization-induced mechanical enhancement of spider silk fibers.


---

## Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

### (a) Papers published in peer-reviewed journals (N/A for none)

Received | Paper

**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

---

### (b) Papers published in non-peer-reviewed journals (N/A for none)

Received | Paper

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

---

### (c) Presentations

**Number of Presentations:** 0.00

---

### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

---

## Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

---

## (d) Manuscripts

Received Paper

**TOTAL:**

**Number of Manuscripts:**

---

## Books

Received Paper

**TOTAL:**

## Patents Submitted

---

## Patents Awarded

## Awards

## Graduate Students

| NAME | PERCENT_SUPPORTED |
| --- | --- |

**FTE Equivalent:**
**Total Number:**

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
| --- | --- |

**FTE Equivalent:**
**Total Number:**

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED |
| --- | --- |

**FTE Equivalent:**
**Total Number:**

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
| --- | --- |

**FTE Equivalent:**
**Total Number:**

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

| | |
| --- | --- |
| The number of undergraduates funded by this agreement who graduated during this period: ...... | 0.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... | 0.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ...... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... | 0.00 |

## Names of Personnel receiving masters degrees

NAME

**Total Number:**

## Names of personnel receiving PHDs

NAME

**Total Number:**

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
|---|---|
| David Breslauer | 0.42 |
| Brendan Turner | 0.92 |
| **FTE Equivalent:** | **1.34** |
| **Total Number:** | **2** |

## Sub Contractors (DD882)

## Inventions (DD882)

## Scientific Progress

See Attachment

## Technology Transfer

**Investigating the Mechanisms and Potential of Silk Fiber Metallization**

Refactored Materials, Inc.

Grant W911NF-12-1-0200

Final Report

June 1, 2012 – June 30, 2013

**Table of Contents**

## Statement of Problem Studied

The metallization of fibers and textiles using Atomic Layer Deposition (ALD) has been of increasing interest for its ability to create novel material surface properties, create conductive materials, and otherwise functionalize materials. In 2009, it was shown that through modification of the ALD process, metal elements could be infiltrated within (rather than simply coating) biological materials. This metal infiltration was shown to dramatically enhance the mechanical properties of biological materials[1]. Native spider silk fibers are unparalleled in their combination of mechanical strength and strain, and these fibers exhibited >2-fold increase in strain to breakage, and >4.5-fold increase in strength when infiltrated with zinc, titanium, or aluminum. Unfortunately, the mechanisms leading to this mechanical improvement, and the limits thereof, have been entirely unexplored. This is due to an inability to replicate to the initial results of the 2009 work by independent labs. We sought to replicate the original work, and to investigate the molecular mechanisms underlying the metallization-induced mechanical enhancement of spider silk fibers.

## Summary of Most Important Results

*Summary*

- Built a custom, in-house ALD for rapid iteration of experiments
- The use of titanium had to be abandoned because of consistent solidification of the precursor
- Metallization led to inconsistent changes in spider silk mechanical properties with infiltration conditions
- We were unable to reproduce results from Lee *et al*.[1]
- We are continuing to address subtle discrepancies between the experiment conditions of Lee *et al.* and our own

*ALD Design, Construction, and Testing*

We designed a custom ALD system for the metal infiltration of biological materials. Although we were able to perform preliminary studies in university labs on commercial reactors, this was impractical moving forward because these tools are generally reserved for ultra-clean semiconductor processes where contamination with non-standard materials (such as protein) is a major concern. Furthermore, ALD systems are in high demand and the long process times required by the metal infiltration process (>12 hours) makes scheduling shared tools impractical and very expensive. Combining our own knowledge of ALD systems with the guidance of Professor Jesse Jur of North Carolina State University, an expert in ALD design and fiber and textiles coating processes[2-6], we built the ALD system shown in Figure 1. An ALD system is a fairly simple tool, consisting of a heated deposition chamber, heated precursor source cylinders and plumbing, a vacuum pump, a mass flow controller for carrier gas, solenoid ALD valves, pump valve, pressure sensors, temperature sensors, and controller software. These components all enable the regulation of conditions in the infiltration chamber, such that precursors can be sequentially pulsed in and pumped out at controlled pressures and temperatures. Our ALD system is similar to the Cambridge Nanotech Savannah 100, but with a larger sample chamber in order to accommodate spools of fiber.

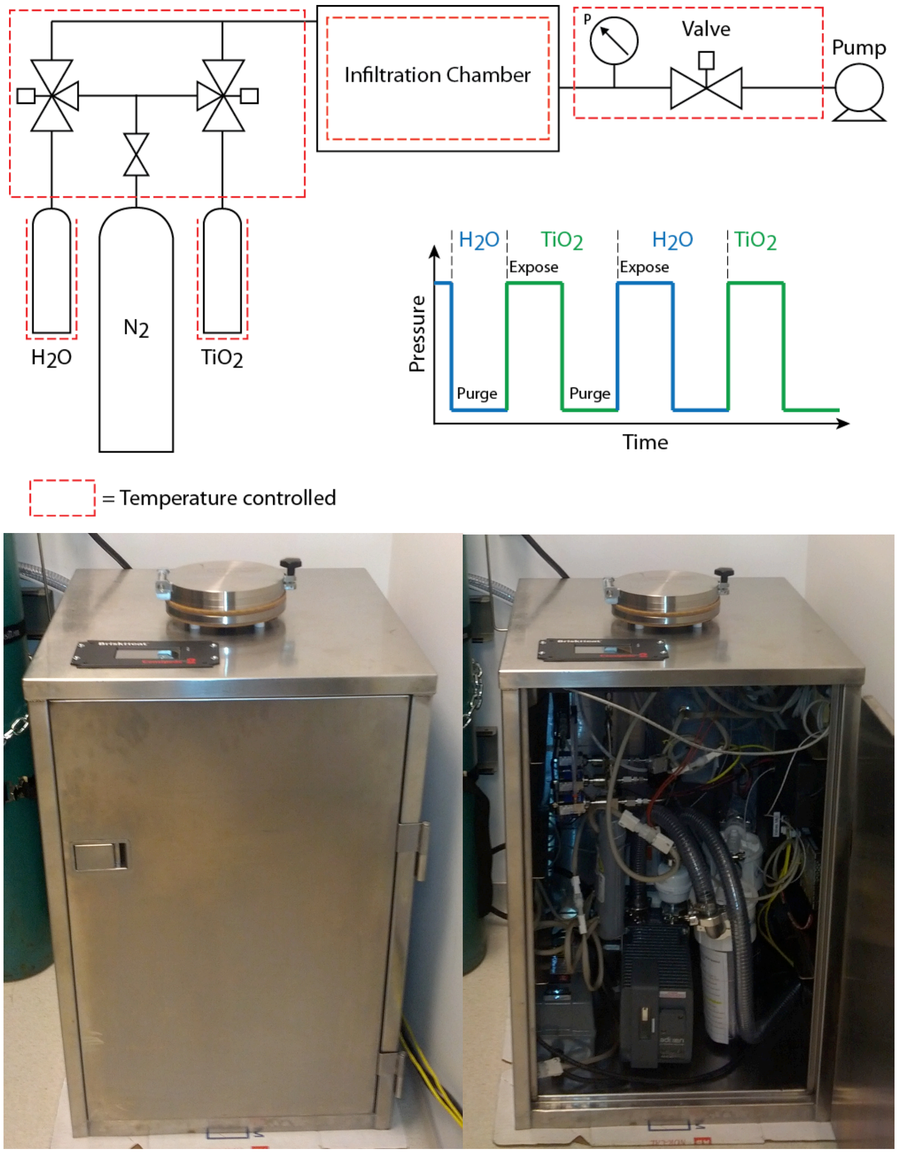



**Figure 1.** (top) Schematic of a two-precursor ALD system. The infiltration chamber holds the fibers, and is alternately filled and purged with water vapor and precursor (inset graph). Various components are temperature and pressure regulated. (bottom) A picture of our in house ALD system used for these experiments. The entire system is controlled by custom LabView software.

With the assistance of Professor Jur, we used ellipsometry to confirm that the system functions as expected for the deposition of both titanium oxide and aluminum oxide. Whereas both precursors functioned properly in an ALD process, when using the modified metal infiltration process as outlined by Lee *et al*., the titanium isopropoxide (TIP) precursor repeatedly solidified. It appears the TIP experienced an irreversible phase change; though as it was heated to 80 ˚C, beyond its melting point of 17 ˚C, the cause of this phase change is unknown. The authors of the original work informed us that this is a problem they also experienced randomly. After substantial troubleshooting, TIP experiments were put on hold in order to focus on experiments with the trimethylaluminum (TMA) precursor, which had led to similar final results as TIP in the original work.

*Spider Silk Fiber Reeling and Testing*

Single major ampullate fibers were continuously reeled from $CO_2$-anesthetized *Nephila Clavipes* spiders imported from Florida. Reeling was performed at 1 cm/s.

All fiber samples were tested using a custom tensile tester consisting of a linear actuator and strain gauge. Fiber samples were mounted to paper frames using Superglue. The paper frame was alligator-clipped into the tensile tester and the sides of the paper frame were cut prior to testing. All samples had a gauge length of 5.75 mm and were tested at a strain rate of 1% / second.

*Infiltration Methodology*

The $Al_2O_3$ metal infiltration process from the Lee *et al*. consists of the following sequence of operation repeated over many cycles:

| | **Temperature** (˚C) | | **Time** (s) | | |
|---|---|---|---|---|---|
| | Precursor | Chamber | Pulse | Exposure | Purge |
| (1) TMA | 20 | 70 | 0.3 | 30 | 30 |
| (2) H2O | 20 | 70 | 1.5 | 40 | 40 |

A pulse refers to the opening of the ALD valve, releasing the precursor into the $N_2$ carrier gas and the downstream sample. Exposure refers to closing the vacuum valve such that the precursor does not flow through the chamber but rather accumulates. Purge refers to opening the vacuum valve and evacuating the chamber.

Lee *et al*. performed the metal infiltration process in a Cambridge Nanotech Savannah 100 ALD designed for 100 mm wafers. Our chamber has roughly 3x the internal volume of the Savannah 100 system so as to accommodate fiber spools. Consequently the baseline pulse time was tripled to achieve comparable precursor concentration during the hold step. “3xP” (below) refers to a 0.9 s / 4.5 s pulse for TMA and $H_2O$ respectively.

On the recommendation of Prof. Jesse Jur, we further modified the ALD system and the process to allow for the option of a hold step instead of an exposure step. Most ALD systems continuously flow $N_2$ carrier gas during runs. This results in the pressure continuously increasing during the exposure step and the precursor being continuously diluted. In a hold step, the $N_2$ carrier gas is valved off after 1.5 s. This allows the precursor pulse to be completely carried into the chamber. The chamber is then sealed such that the pressure and precursor concentration stay constant during the entire hold step. Professor Jur has repeatedly shown this to be a simple and effective process modification to achieve deep metal infiltration into fibrous materials with many fewer cycles[2-6]. “3xH” (below) refers to a 90 s / 120 s hold for TMA and $H_2O$, respectively.

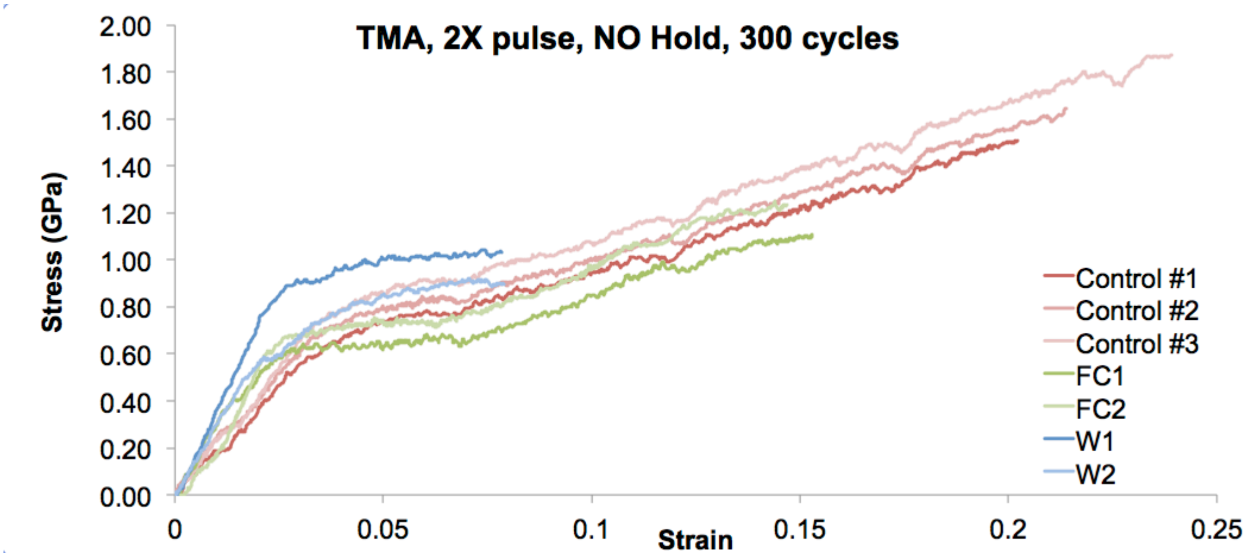
For certain experiments, samples were mounted at multiple locations in the ALD chamber to test for uniformity differences in the chamber:

- “FC” refers to fibers mounted at the front (upstream) location in the chamber on a paper clip.
- “BC” refers to fibers mounted at the back (downstream location in the chamber on a paper clip.
- “W” refers to fibers mounted in the center of the chamber on a custom white Teflon spool. Later experiments distinguished between WF – front/upstream side of spool and WB – back/downstream side of spool.

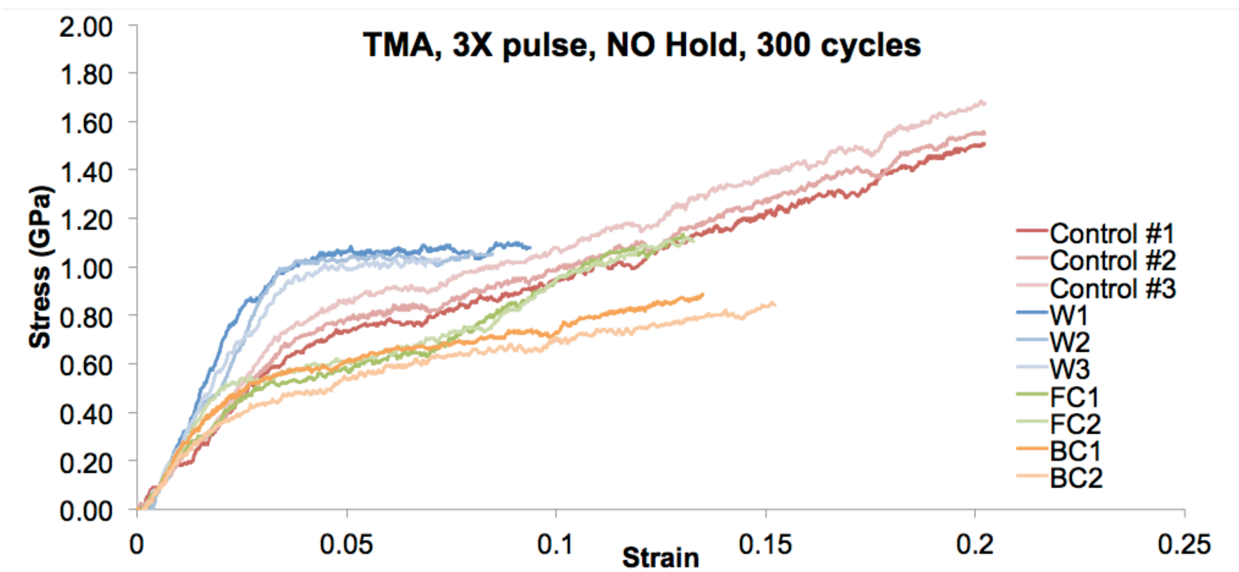
Lastly, “split runs” had a change in the order of the pulses. Instead of alternating TMA and $H_2O$ in a cycles, many cycles of $H_2O$ were followed by many cycles of TMA.

*Experimental Results*

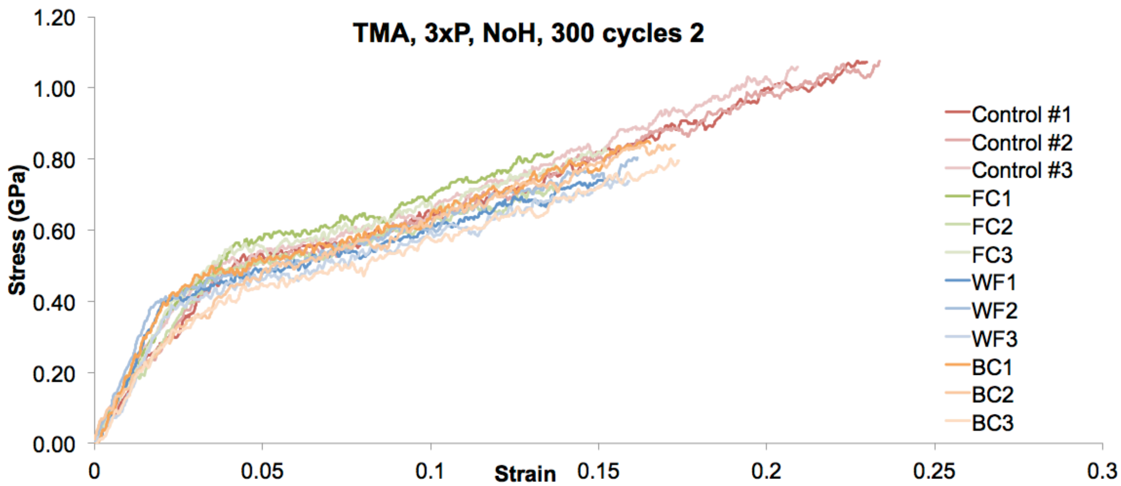
- TMA precursor, 2x pulse time, 300 cycles
    - Center (“W”) samples showed an increase in modulus and yield point as well as the largest decrease in breaking strain. All treated fibers showed significant decreases in breaking strain.



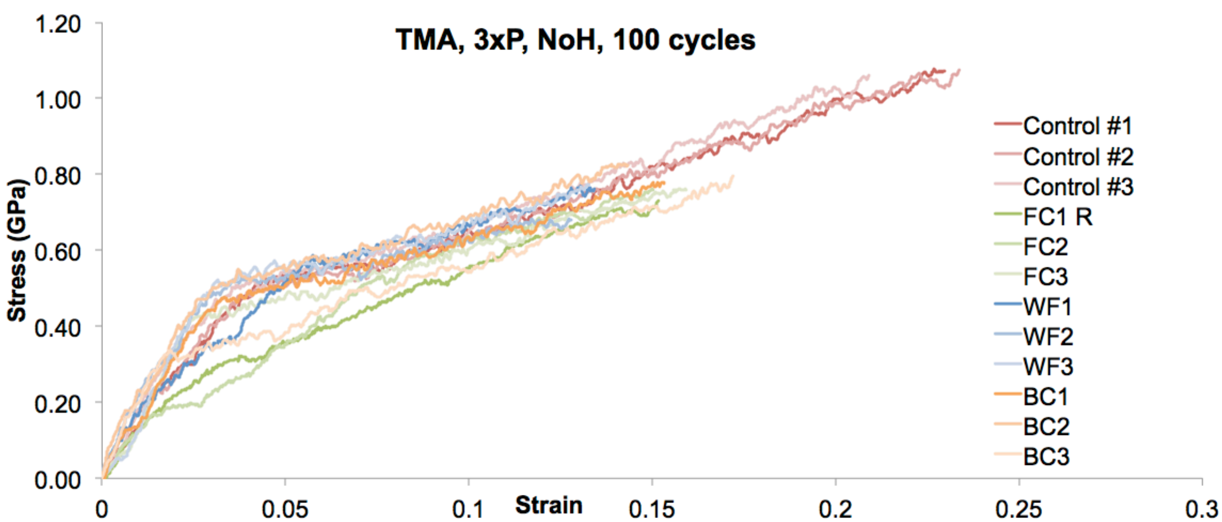

- TMA precursor, 3x pulse time, 300 cycles
    - Center (“W”) fibers again showed a slight increase in modulus and yield point and decrease in breaking strain. Front and Back fibers showed lower yield point.



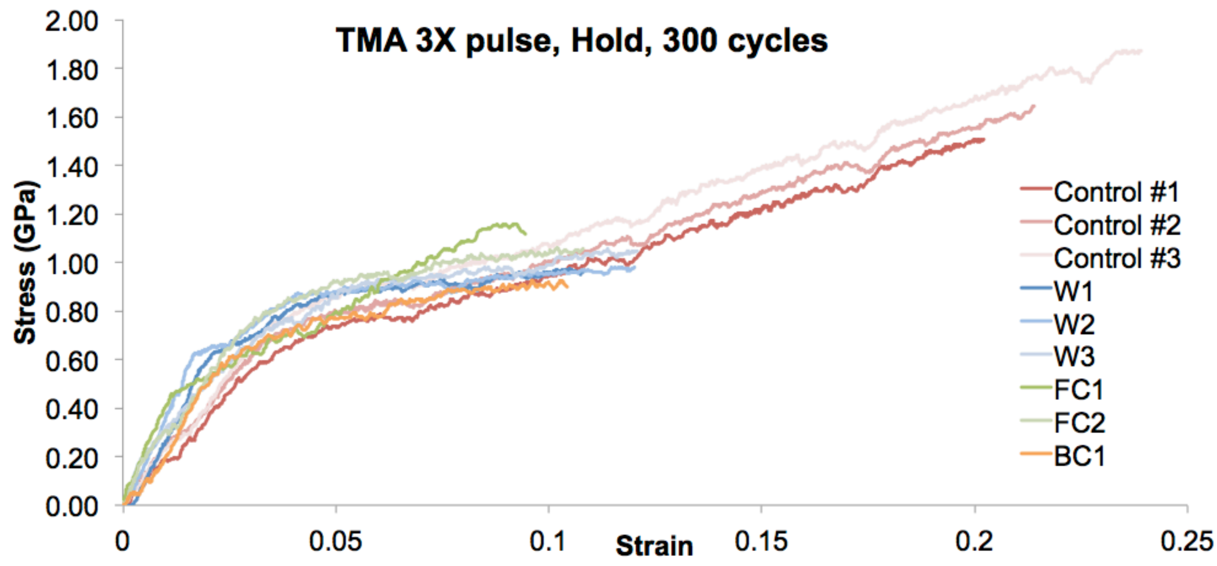

    - Repeating these conditions failed to reproduce the initial increase in modulus and yield.



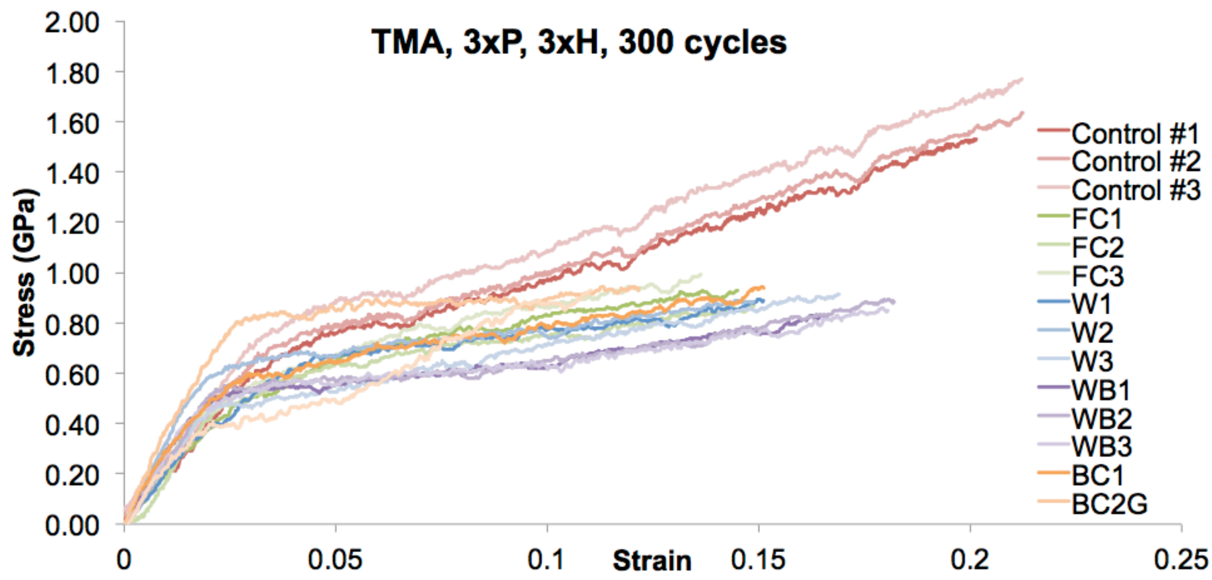

- TMA precursor, 3x pulse time, 100 cycles
    - Lowering the cycle count produced similar results to 300 cycles (above).



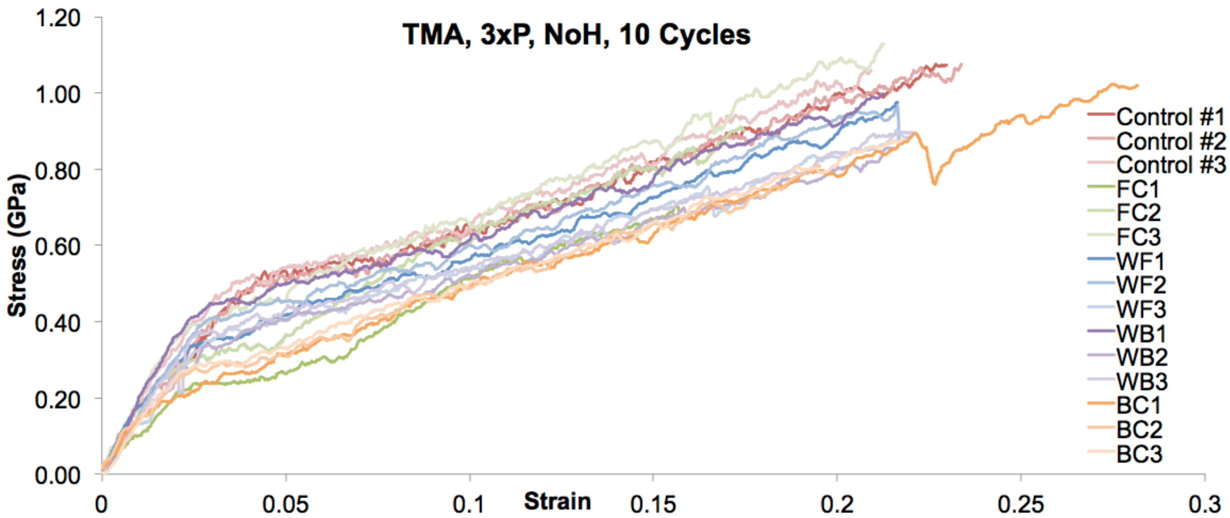

- TMA precursor, 3x pulse time, 1x Hold, 300 cycles
    - A hold step was added in order to attempt to improve the amount of metal infiltrated in the fibers. All fibers showed consistently lower breaking strain as compared to controls.



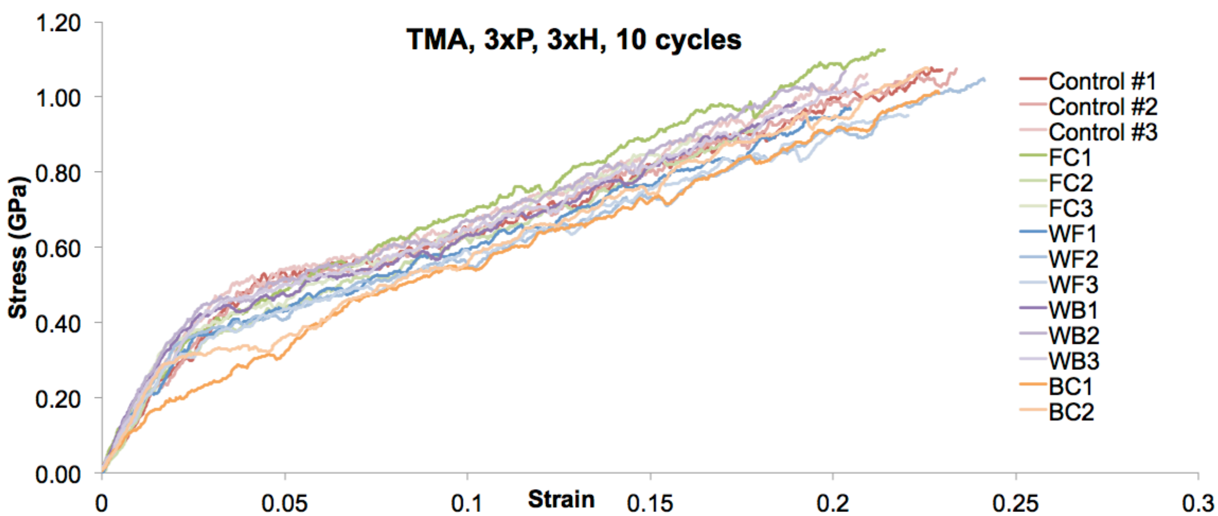

- TMA precursor, 3x pulse time, 3x Hold, 300 cycles
    - Increasing the hold time lowered the yield point and lowered the post-yield slope of the stress-strain curve.



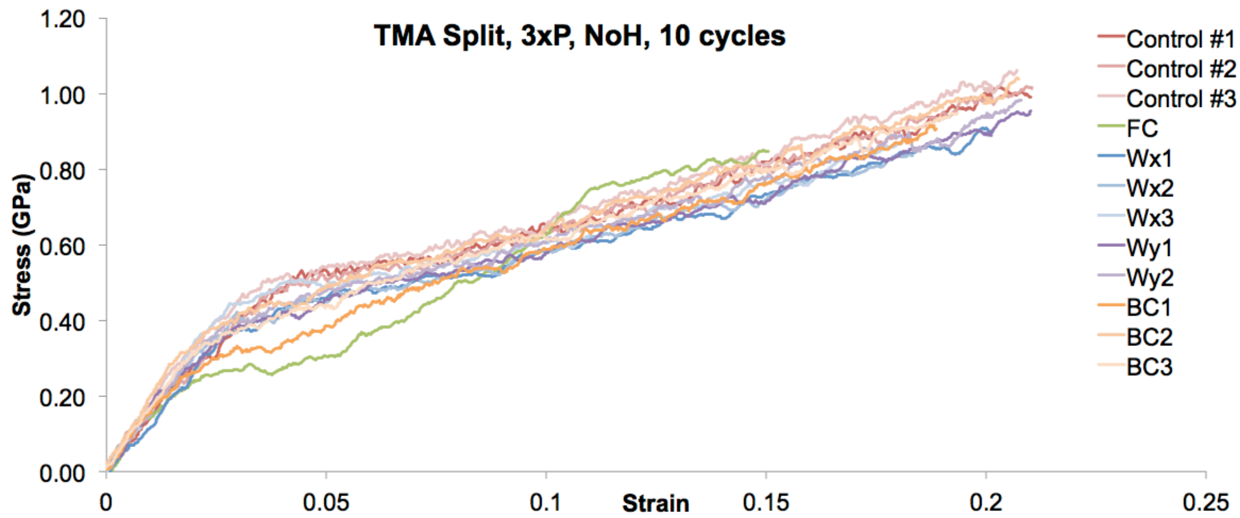

- TMA precursor, 3x pulse time, No Hold, 10 cycles
    - The cycle count was decreased to try and determine intermediate effects during the process. Decreases in yield point became less consistent and fibers retained their high breaking strain.



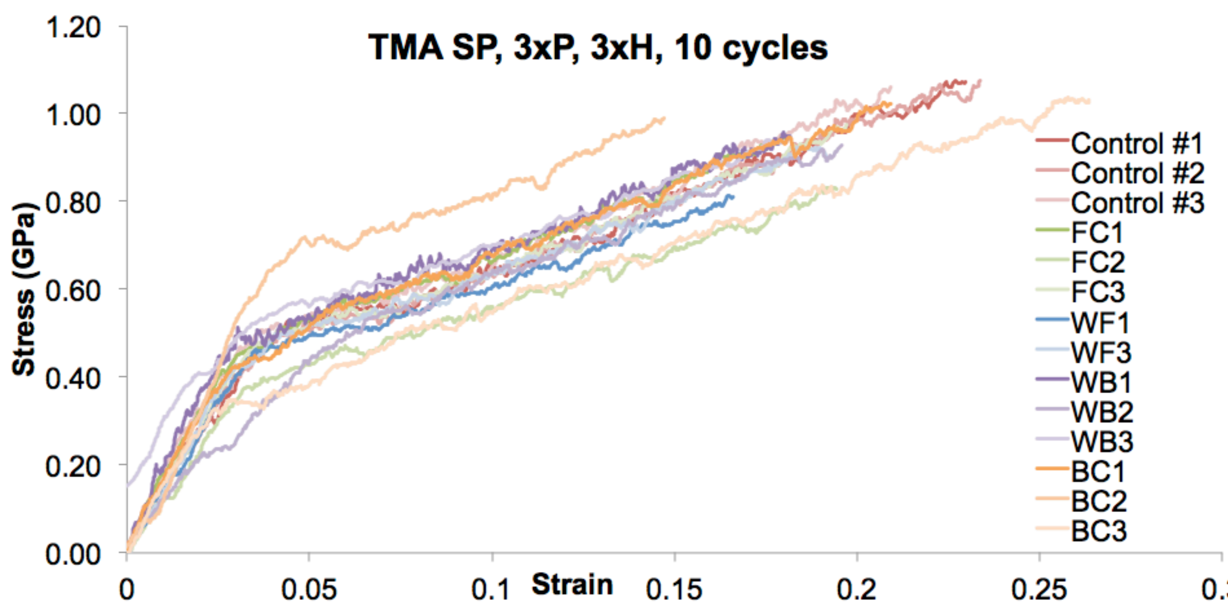

- TMA precursor, 3x pulse time, 3x Hold, 10 cycles
  - Some fibers exhibited decreases in yield point.




- TMA precursor, Split run, 3x pulse time, 10 cycles
  - Some fibers exhibited decreases in yield point.




- TMA precursor, Split run, 3x pulse time, 3x Hold, 10 cycles
  - A split run with a 3x hold step seemed to produce varied results, without any conclusive trends.




*Conclusions*

Initial results showing an increase in modulus of the fibers were promising, but failed to be repeatable. We suspect that the initial modulus increase was due to a metal coating on the fibers that dominated the fiber tensile properties. For the most part, the metallization process weakened the fibers. It is unclear why our process was not repeatable and why longer processes weakened fibers, but further investigation into the effect of each parameter of the process space (temperature, pressure, etc) on silk fiber mechanical properties is under way to elucidate whether the metal infiltration process is actually feasible. At this stage, mechanical property measurements will no longer be sufficient as an assay for the effect of the metal infiltration process. Without the dramatic changes observed by Lee *et al.*, next steps would involve assays such as EDX to observe how much metal penetrates the fiber.

We are continuing to explore key variables that are different between our work and that of Lee *et al.* Primarily, our spider silk fibers were reeled from *Nephila clavipes* spiders and, in the original work, major ampullate silk from *Araneous diadematus* were collected at natural spinning speeds. Given the fundamental similarities in sequence and structure of these two different silk fibers, it is difficult to speculate as to how this would make a difference in the process but it is a simple experiment to perform. Additionally, due to the solidification of the TIP, we were only able to study the TMA precursor. Whereas the original authors observed equivalent success with TMA, it will be necessary to replicate their results with TIP in order to fully understand the process.

It is unlikely that the work of Lee *et al*. is irreproducible, but we suspect that proper metal infiltration of fibers requires an extremely specific process window that even the original authors do not entirely understand. This project allowed us to construct an ALD system, thoroughly learn the process space around metal infiltration, and baseline the process. Given the lack of mechanical improvements of the fibers by a nearly duplicate process outlined by Lee *et al.*, a more in depth and systematic approach will be required to investigate the metal infiltration process.

## Personnel

David Breslauer, PhD
Brendan Turner, MS
Jesse Jur, PhD (Consultant)

## Interactions

Refactored Materials is committed to engaging with the academic and industrial community. Professor Jesse Jur (NCSU) consulted on this project. Our scientific advisory board includes Prof. David Kaplan (Tufts), Prof. Sam Hudson (NCSU), Prof. Chris Voigt (MIT), Prof. Travis Bayer (Oxford), and Prof. Susan Muller (UC Berkeley), all of whom we interact with regularly. We are industrial members of SynBERC, the NSF Synthetic Biology Engineering Research Center, as well as the Synthetic Fibers and Yarns Association. We regularly attend and participate in the Silk workshops when they are held.

## Bibliography

(1) Lee, S. M.; Pippel, E.; Gosele, U.; Dresbach, C.; Qin, Y.; Chandran, C. V.; Brauniger, T.; Hause, G.; Knez, M. *Science* **2009**, *324*, 488.

(2) Gong, B.; Peng, Q.; Jur, J. S.; Devine, C. K.; Lee, K.; Parsons, G. N. *Chem Mater* **2011**, *23*, 3476.

(3) Hyde, G. K.; Scarel, G.; Spagnola, J. C.; Peng, Q.; Lee, K.; Gong, B.; Roberts, K. G.; Roth, K. M.; Hanson, C. A.; Devine, C. K.; Stewart, S. M.; Hojo, D.; Na, J. S.; Jur, J. S.; Parsons, G. N. *Langmuir* **2010**, *26*, 2550.

(4) Jur, J. S.; Parsons, G. N. *Acs Appl Mater Inter* **2011**, *3*, 299.

(5) Jur, J. S.; Spagnola, J. C.; Lee, K.; Gong, B.; Peng, Q.; Parsons, G. N. *Langmuir* **2010**, *26*, 8239.

(6) Spagnola, J. C.; Gong, B.; Arvidson, S. A.; Jur, J. S.; Khan, S. A.; Parsons, G. N. *J Mater Chem* **2010**, *20*, 4213.